Reactions of Ketene

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Ketene, the inner anhydride of acetic acid, is manufactured by the pyrolysis of acetic acid and acetone. Commercially it is used principally in the production of acetic anhydride and, to a lesser extent, diketene. The discovery and development of new catalysts for reactions with ketene have now led to the manufacture of β-lactones and enol acetates from carbonyl compounds and ketene.

Ketene can be prepared in the laboratory by the pyrolysis of acetone (1).

Recently Kung (2) described the condensation of ketene, $CH_2=C=O$, with formaldehyde and acetaldehyde in the presence of Friedel-Crafts type catalysts to form propionolactone and β-butyrolactone, respectively.

A similar condensation with ketene and furfural and ketene and benzaldehyde was reported by Hurd in 1933 (3) in which the β-lactone decarboxylation products, α-vinylfuran and styrene, re-

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spectively, were isolated.

Gwynn and Degering (4) in 1942 discovered that enol acetylation with ketene was accomplished in good yields by using acid esterification catalysts. Acetone and ketene reacted in the presence of sulfuric acid catalyst to form isopropenyl acetate.

$$CH_3COCH_3 \rightleftharpoons CH_2=C(OH)CH_3 +$$
$$CH_2=C=O/H_2SO_4 \longrightarrow$$
$$CH_2=C(CH_3)OCOCH_3$$
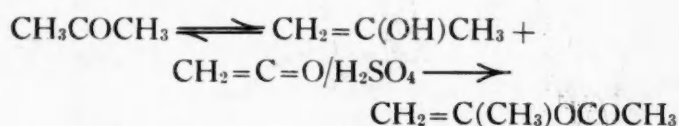
With the advent of the work of Degering (4) and Kung (2) a renewed interest has been taken in the utilization of ketene in the synthesis of organic compounds.

In the author's laboratories the condensation of ketene with itself and with carbonyl compounds—aldehydes, ketones, diketones, keto esters, aromatic aldehydes and ketones, and unsaturated aldehydes and ketones—has been investigated. Other catalysts have also been found which are suitable for the condensation, and in some instances they are

superior to the Friedel-Crafts type of catalysts for the formation and isolation of β-lactones. Aldehydes and α,β-unsaturated aldehydes and ketones were also enol acetylated.

Diketene

The dimerization of ketene should be considered in a study of the condensation of ketene with carbonyl groups. Of the three structures commonly assigned to diketene, β-vinylacetolactone has been chosen as representing the product of the condensation of the carbon-to-carbon double bond of one ketene molecule with the carbonyl group of a second ketene molecule to form a β-lactone.
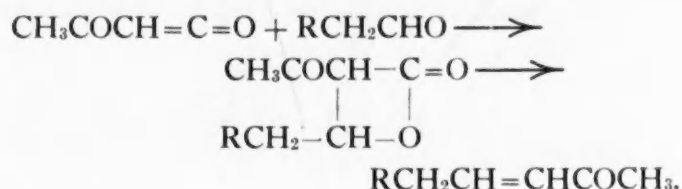
$$CH_2=C=O + CH_2=C=O \xrightarrow[\text{No catalyst}]{50\ C}$$
$$CH_2=CCH_2C=O$$
$$\underset{\llcorner O \lrcorner}{}$$

$$CH_3COCH=C=O \qquad\qquad CH_2=CCH_2C=O$$
$$\underset{\llcorner O \lrcorner}{}$$
$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$

$$CH_3C=CHC=O$$
$$\underset{\llcorner O \lrcorner}{}$$
$$\text{III}$$
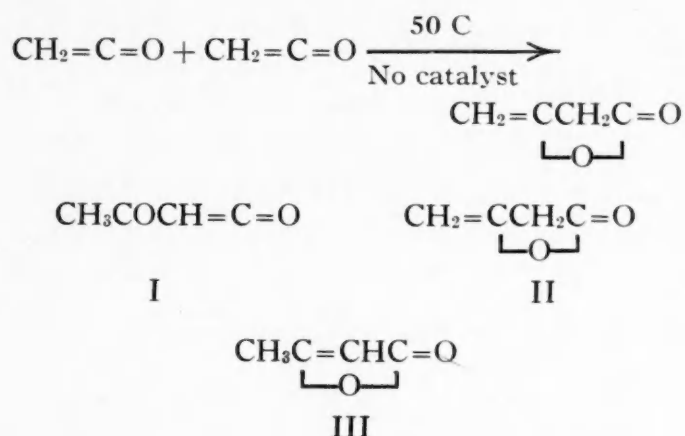
Although many investigators show a preference for either β-vinylacetolactone (II) or β-crotonolactone (III) as representing the structure of diketene, it is interesting to note that diketene does not form β-alkoxy compounds with alcohols which is characteristic of the β-lactones.

β-Butyrolactone is produced by the hydrogenation of diketene with Raney nickel catalyst at 60 to 70 C and 300 to 500 pounds per square inch in the presence of an equal or larger volume of diluent. In continuous hydrogenation diketene can be hydrogenated directly to butyric acid.

Ketene and aliphatic aldehydes such as acetaldehyde, propionaldehyde, and butyraldehyde react without catalyst to form α,β-unsaturated ketones.

$$2CH_2=C=O + RCH_2CHO \longrightarrow$$
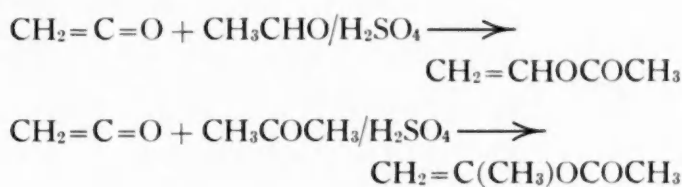$$RCH_2CH=CHCOCH_3 + CO_2$$
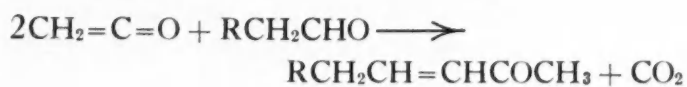
Actually the ketene dimerizes to diketene and as such reacts with the aldehyde to form a β-lactone which decarboxylates upon heating to form the α,β-unsaturated methyl ketone (5).

$$CH_3COCH=C=O + RCH_2CHO \longrightarrow$$
$$CH_3COCH-C=O \longrightarrow$$
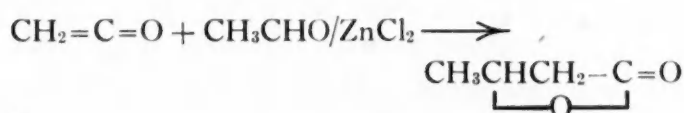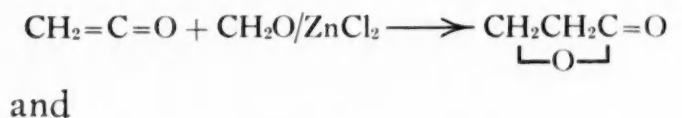$$\underset{\mid\qquad\mid}{RCH_2-CH-O}$$
$$RCH_2CH=CHCOCH_3.$$

A similar condensation reaction is not observed with ketones. Ketene and acetone do react, however, in the absence of a catalyst at elevated temperatures, to form small amounts of isopropenyl acetate in addition to diketene.

With catalysts such as sulfuric acid (6), p-toluenesulfonic acid, and particularly with acetylsulfoacetic acid in concentrations of 0.01 to 0.1 % and at 40 to 80 C, the corresponding enol acetates are formed.
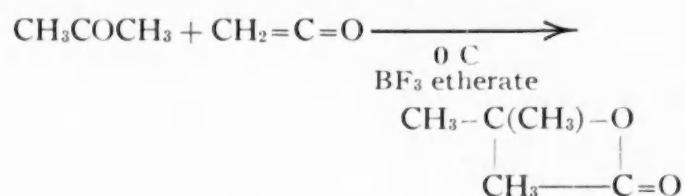
$$CH_2=C=O + CH_3CHO/H_2SO_4 \longrightarrow$$
$$CH_2=CHOCOCH_3$$

$$CH_2=C=O + CH_3COCH_3/H_2SO_4 \longrightarrow$$
$$CH_2=C(CH_3)OCOCH_3$$

In the presence of suitable condensation catalysts, aldehydes and ketones condense with ketene to form β-lactones. Some of the better catalyst materials include boric acid, triacetyl borate, mercuric chloride, zinc chloride, zinc thiocyanate, magnesium perchlorate, and boron trifluoride etherate.

$$CH_2=C=O + CH_2O/ZnCl_2 \longrightarrow CH_2CH_2C=O$$
$$\underset{\llcorner O \lrcorner}{}$$

and

$$CH_2=C=O + CH_3CHO/ZnCl_2 \longrightarrow$$
$$CH_3CHCH_2-C=O$$
$$\underset{\llcorner\quad O\quad\lrcorner}{}$$

Catalysts suitable for use in the condensation of ketene with carbonyl compounds generally fall within the classification of a group of salts which are strongly acid in concentrated aqueous solutions (7). The compounds are capable of forming co-ordination complexes
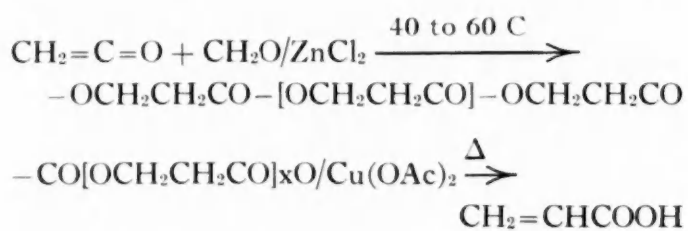
with hydroxy groups and also have a strong catalytic activity towards carbonyl derivatives. These compounds include the borates, aluminates, halides, thiocyanates, nitrates, chlorates, and perchlorates of zinc, tin, mercury, aluminum, lithium, boron, iron, manganese, and cobalt.

With ketones such as acetone and methyl ethyl ketone the reaction is carried out in the presence of excess ketone, which is recovered and recycled.

$$CH_3COCH_3 + CH_2{=}C{=}O \xrightarrow[\text{BF}_3 \text{ etherate}]{0\ C}$$

$$CH_3{-}C(CH_3){-}O$$
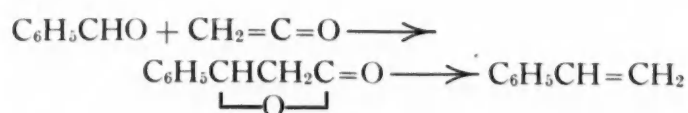$$| \qquad\qquad |$$
$$CH_3{-\!-\!-}C{=}O$$

As the molecular weight increases, the problem of isolating the lactone becomes more difficult because of a tendency to decarboxylate. However, once the β-lactones are isolated in the pure state, they are stable at room temperature.

If an unsaturated acid is desired as the final product, the reaction between ketene and the carbonyl compound is carried out at 40 to 60 C to give a low molecular weight linear polyester of the β-lactone directly. This linear polyester is then depolymerized by distillation to form the α,β-unsaturated acid (10, 11).

$$CH_2{=}C{=}O + CH_2O/ZnCl_2 \xrightarrow{40\ to\ 60\ C}$$

$${-}OCH_2CH_2CO{-}[OCH_2CH_2CO]{-}OCH_2CH_2CO$$

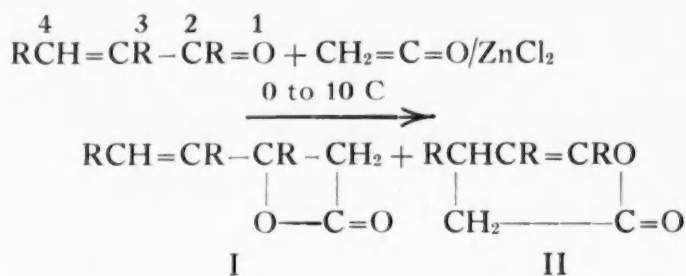$${-}CO[OCH_2CH_2CO]xO/Cu(OAc)_2 \xrightarrow{\Delta}$$
$$CH_2{=}CHCOOH$$

Benzaldehyde and acetophenone react with ketene, boric acid and zinc chloride being used as catalysts at 0 to 10 C. Decarboxylation gives styrene and α-methylstyrene respectively in good yields.

$$C_6H_5CHO + CH_2{=}C{=}O \longrightarrow$$
$$C_6H_5CHCH_2C{=}O \longrightarrow C_6H_5CH{=}CH_2$$
$$\underset{\llcorner O \lrcorner}{}$$

Unsaturated aldehydes and ketones can react with ketene to give a variety of products. In the presence of suitable condensation catalysts, ketene adds both 1,2 and 1,4 to form β(I)- and δ(II)-lactones.
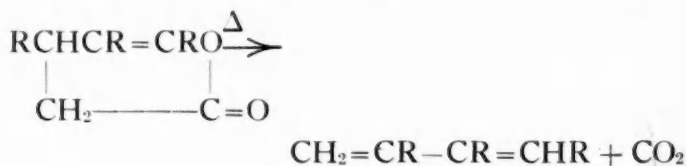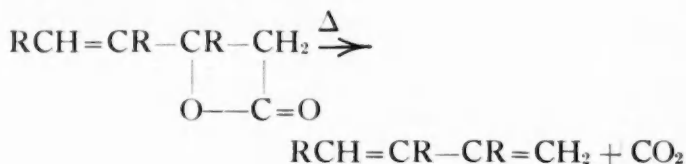
$$\overset{4}{R}CH{=}\overset{3}{C}R{-}\overset{2}{C}R{=}\overset{1}{O} + CH_2{=}C{=}O/ZnCl_2$$
$$\xrightarrow{0\ to\ 10\ C}$$

$$RCH{=}CR{-}CR{-}CH_2 + RCHCR{=}CRO$$
$$\quad | \quad | \qquad\qquad | \qquad\qquad |$$
$$\quad O{-\!-}C{=}O \qquad CH_2{-\!-\!-\!-}C{=}O$$
$$\quad\quad \text{I} \qquad\qquad\qquad \text{II}$$

R can be hydrogen, alkyl, or aryl.

β-Lactones

The β-lactones are decarboxylated by pyrolyzing or heating at temperatures above 100 to 120 C to form diene derivatives. d-Lactones decarboxylate at slightly higher temperatures and also form diene derivatives.

$$RCH{=}CR{-}CR{-}CH_2 \xrightarrow{\Delta}$$
$$\quad\quad | \quad |$$
$$\quad\quad O{-\!-}C{=}O$$
$$\qquad\qquad RCH{=}CR{-}CR{=}CH_2 + CO_2$$

$$RCHCR{=}CRO \xrightarrow{\Delta}$$
$$| \qquad\qquad |$$
$$CH_2{-\!-\!-\!-}C{=}O$$
$$\qquad\qquad CH_2{=}CR{-}CR{=}CHR + CO_2$$

β-Lactones are usually formed in the ratio of 10 to 1 of the δ-lactones as calculated from the yield of olefinic decomposition products obtained from the condensation of crotonaldehyde with ketene. If a doubly unsaturated acid is the desired product, the condensation is carried out at 40 to 50 C, and a product is obtained comprising largely the linear polyesters of the lactones. Destructive distillation at reduced pressure results in the formation of the doubly unsaturated acid. Sorbic acid is manufactured in 70 to 80% yields in this way from crotonaldehyde and ketene.
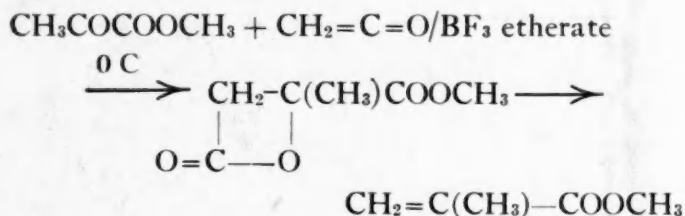
With enol esterification catalysts at 50 to 80 C, the corresponding acetoxy dienes are formed. For example, 1-acetoxy-1,3-butadiene is produced by the reaction of ketene with crotonaldehyde in the presence of sulfuric acid at 60 to 80 C.

$$CH_2=C=O + CH_3CH=CHCHO/H_2SO_4$$
$$\xrightarrow{60 \text{ to } 80 C} CH_2=CHCH=CHOCOCH_3$$
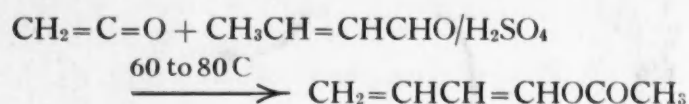
Ketene condenses with diketones to form the mono- and di-β-lactones. In the absence of excess ketene the decarboxylation products indicate the formation of both the mono- and di-β-lactones (8, 9).
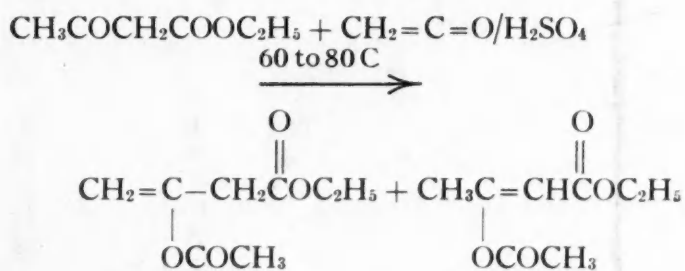
Keto Esters

Methyl pyruvate, ethyl acetoacetate, and methyl levulinate also react with ketene under condensation and enol acetylation conditions. Methyl pyruvate reacts with ketene to form a β-lactone, which is then decarboxylated to form methyl methacrylate.

$$CH_3COCOOCH_3 + CH_2=C=O/BF_3 \text{ etherate}$$
$$\xrightarrow{0 C} \begin{array}{c} CH_2-C(CH_3)COOCH_3 \\ | \quad\quad | \\ O=C\!-\!\!-O \end{array} \longrightarrow$$
$$CH_2=C(CH_3)-COOCH_3$$

Ethyl acetoacetate and methyl levulinate undergo the same condensation to form unsaturated esters. As the carbonyl group is removed from the carboxyl group, the ease of formation of the β-lactone increases, and higher yields of the unsaturated esters are obtained. Hydroxydicarboxylic acids can be formed by hydrolysis of the crude lactone, and with alcohols the corresponding alkoxydicarboxylic acid diester is produced.
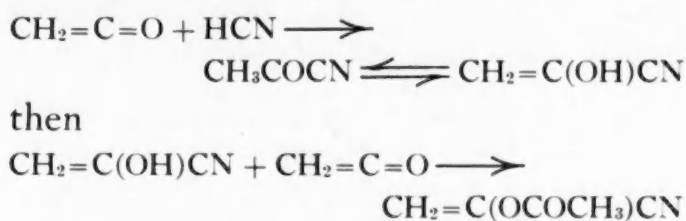
Enol acetylation of methyl pyruvate gives a low yield of methyl α-acetoxyacrylate. Ethyl acetoacetate and ethyl levulinate leads to a mixture of isomers —e.g., with acetoacetic ester.

$$CH_3COCH_2COOC_2H_5 + CH_2=C=O/H_2SO_4$$
$$\xrightarrow{60 \text{ to } 80 C}$$
$$\begin{array}{cc} \quad\quad O & \quad\quad O \\ \quad\quad \| & \quad\quad \| \\ CH_2=C-CH_2COC_2H_5 + CH_3C=CHCOC_2H_5 \\ | & | \\ OCOCH_3 & OCOCH_3 \end{array}$$

The enol acetates of acetoacetic ester rearrange on prolonged heating in the presence of acid catalysts to form ethyl diacetylacetate.

The enol acetates of the ketoesters can be copolymerized with vinyl monomers in the presence of peroxide catalysts to give clear, colorless resins.

The reaction of ketene with hydrocyanic acid (12, 13) shows the formation of an enolizable ketonitrile which is subsequently acetylated to form the enol acetate (14). The reactions which occur are represented by the equations.

$$CH_2=C=O + HCN \longrightarrow$$
$$CH_3COCN \rightleftharpoons CH_2=C(OH)CN$$

then

$$CH_2=C(OH)CN + CH_2=C=O \longrightarrow$$
$$CH_2=C(OCOCH_3)CN$$

In addition to α-acetoxyacrylonitrile a small amount of the dimer of pyruvonitrile is also formed.

$$2CH_3COCN \longrightarrow CH_3CO_2C(CN)_2CH_3$$
$$\text{\(\alpha\)-acetoxyisosuccinic dinitrile}$$
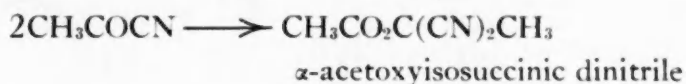
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